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Mass Spectrometric Analyses of Bubbles in Fluoride Glasses

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Gas bubbles in fluorozirconate glasses lead to high losses in otherwise ultra-low loss optical fibers. This report summarizes mass spectrometer analyses performed to characterize these bubbles. All samples were provided by the Naval Research Laboratory. The data suggests the exsolution and complete resorption of an unidentified gas species leaving only residual traces of relatively inert species - N_2, Ar, and possibly CO_2.

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Block 18 - Subject Terms

Gas bubbles in preforms and fiber
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Summary

The presence of gas bubbles in preforms and fiber made of fluorozirconate glasses leads to high losses in otherwise ultra-low loss optical fibers. This report summarizes the results of mass spectrometer analyses performed to characterize the bubbles which occur in these glasses. All samples submitted for analyses were provided by the Naval Research laboratory. The data suggests the exsolution and complete resorption of an unidentified gas species leaving only residual traces of relatively inert species - N_2, Ar, and possibly CO_2.

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Analytical Capability

The mass spectrometer - ultrahigh vacuum system used to perform these analyses has been described elsewhere.[1] Since the original publication, the analytical capabilities of that instrument have evolved to yield the following routine analytical capability. These minimum detectable quantities of gases usually seen during the analysis of bubbles in commercial soda-lime silicate glasses are expressed as a pressure-volume product.

H_2 - 25×10^{-6} Pascal-liter
He, CO, CH_4 - 5×10^{-6}
N_2 - 2×10^{-6}
H_2O, CO_2, Ar - 0.5×10^{-6}
O_2, SO_2, COS, H_2S - 0.2×10^{-6}

To provide a better feel for the quantities of gas involved, the above are related to the quantities of gas contained in bubbles whose diameters range from 100 down to 20 micron (10^{-6} meter).

Bubble Diameter (10^{-6} meter)	Gas Quantity @ 30 kilo-pascal Internal Pressure (10^{-6} Pa l)	Minimum Detectabilities (10^{-6} Pa l)
		25 (H_2)
100	17	
		5 (He, CO, CH_4) 2 (N_2)
40	1	
		0.5 (H_2O, CO_2, Ar) 0.2 (O_2, SO_2, COS, H_2S)
20	0.13	

As the above table demonstrates, the system's routine minimum detectabilities for gases (save H_2) are such that analyses of bubbles down to 100 micron (10^{-4} meter) can be obtained providing their internal pressure is on the order of 30 kilopascal (1/3 atmosphere). Pressures on that order are realized in bubbles in molten soda-lime-silica glasses which contain gases which do not condense, resorb, or otherwise react with the glass as it cools. The gases cited above are those that are typically encountered in the analysis of bubbles associated with the manufacture of soda-lime-silicate glasses. The minimum detectabilities for these or any other gases are determined by the sensitivity of the mass analyzer and the capability of the ultra-high vacuum (uhv) system, the latter controlling the environment in which the analyses are performed. The most abundant background gases in the system are H_2, CO, and CH_4, thus the system is least sensitive to these gases. The system is most sensitive to gases which are not present in the background or for which no conflicting peaks are present, e.g., O_2 and SO_2. The minimum detectability for reactive gases such as H_2O, SO_2, and H_2S are estimated since absolute sensitivities of small quantities of these species are not unequivocally obtained. Similarly, sensitivities for reactive species which may be of particular interest to the Naval Research Laboratory (NRL) such as F_2, HF, or other halogen-containing species will not be known. However, it is expected that these gases will be detectable at levels on the order of 0.2×10^{-6} pascal-liter since no background species or peaks conflicting with these gases exist.

Analyses involving glass systems other than commercial soda-lime-silicates have been performed in this system. They include simulated nuclear waste glasses, B_2O_3 and borosilicate glasses, silicon-silicon dioxide films, phosphate glasses and most

recently (for NRL), fluoride glasses.[2] Beyond the gases cited above, our system has detected the following species in a variety of bubble-in-glass samples: nitrogen oxides, silicon tetrachloride, phosphorus and phosphine, and various hydrocarbons including some containing fluorocarbon radicals.

Sample Analyses

Only four (4) sample lots were submitted over the term of the contract which began in September, 1986 and was to have covered analyses of 35 sample lots. A detailed description of the individual analyses and conditions pertaining to the analyses has been provided in the individual monthly progress reports BNRL/1 (November 13, 1986) through BNRL/7 (June 17, 1987).

The majority of the samples consisted of fluoride glass rod identified by code number only. These cylindrical rod contained a string of bubbles or voids located along the axis of the rod. Bubble size varied widely ranging from a maximum volume over 5 microliters to under 1×10^{-9} liter.

The mass spectrometer analyses consistently found little or no gas left in the rod bubble samples. Some samples (A1 through A4 - Report BNRL/2) contained approximately 100 pascals of N_2, another (RR13 - Report BNLR/4) only 30 pascals of argon - in both cases less than 1/1000 atmosphere internal pressure. Residual amounts of CO_2 and argon were observed during the analyses of several other samples but at levels at which it cannot unequivocally be stated that these gases were present in the bubbles. Definition of the source of the N_2 (A1 - A4) and argon (RR13) cannot be made since the treatment and conditioning of these or any other samples was not revealed. These gases are sparingly soluble and likely either diffused into the bubbles after they were formed or were entrapped during the preparation of the glasses.

The only non-rod sample was a sample identified as "bulk glass" and coded ZF1703 (Report BNLR/4). That sample contained several dozen bubbles whose diameters ranged from 0.01 to 0.05 millimeter (10 to 50 microns). On analysis, quantities of argon were observed that indicated that the internal pressure of those bubbles was on the order of 100,000 pascals (~1 atmosphere).

Discussion

The most significant result of the analyses performed on samples submitted under this contact is the consistent low internal pressure with little if any remaining residual gas(es). If these bubbles were formed by the exsolution of gases or by the reaction of the glasses with the container or the atmosphere over it, those gases have gone back into solution as the glass was cooled. The reactive gases noted by Tran et al[3] or the fluoride species described by Mathew and Doremus[4] are possibilities. No traces of fluoride or chloride species were detected during these analyses even though the mass spectrometer background is relatively clean at the appropriate masses. For that reason, minimum detectabilities for these species should be equivalent to that of the most sensitive species, e.g. O_2 and SO_2 noted earlier.

The data of Shelby and Jewell[5] show that oxygen is another possibility for a very reactive gas species which might be driven out of solution at high temperatures and completely resorbed at low temperatures. As with the halogens, no traces of O_2 were detected during the analyses of glasses submitted under this contract.

Nitrogen and argon, suggested by Tran et al[3] as likely inert atmospheres under which the HF glasses may be prepared, were observed in some of the samples submitted for analyses. In particular argon, the least soluble of the gases examined by Shelby and Jewell[4], was observed at high internal pressures in bubbles in the only bulk glass sample submitted for analysis.

Without knowing the history of the individual samples one can only speculate, however the above results are most likely explained by either of the following. Homogenous or, more likely, heterogenous formation of reactive gas bubbles occurs with the inert species diffusing into the bubbles after they are formed in an initially bubble-free melt. Possible nucleating sites include crucible sidewalls, devitrification and phase separation. Conversely, the presence of microscopic bubbles of the inert or sparingly soluble species may serve as the nucleating sites and remain after the reactive species has gone back into solution.

Conclusion

The mass spectrometer results indicate the exsolution of the reactive gas species while the glasses are molten and subsequent resorption when the glass cools. The presence of small residual amounts of N_2, argon, and/or CO_2 in some of the samples may be due to either of the following reasons. Entrapment of small bubbles during the melting and fabrication of the glasses submitted for analysis. These small bubbles then act as nucleating sites for the release of the reactive species. The alternative is the diffusion of these sparingly soluble species into the bubbles

formed by the exsolution of the reactive species. Although the mass spectrometer background is low and therefore very sensitive to any halogen-containing species or oxygen, no evidence of any putative reactive species was seen indicating that either the exsolved gas(es) are completely resorbed or that another mechanism for the formation of these voids exists.

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